

# Characterization of ferrimagnetic Heisenberg chains according to the constituent spins

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**Abstract.** The low-energy structure and the thermodynamic properties of ferrimagnetic Heisenberg chains of alternating spins  $S$  and  $s$  are investigated by the use of numerical tools as well as the spin-wave theory. The elementary excitations are calculated through an efficient quantum Monte Carlo technique featuring imaginary-time correlation functions and are characterized in terms of interacting spin waves. The thermal behavior is analyzed with particular emphasis on its ferromagnetic and antiferromagnetic dual aspect. The extensive numerical and analytic calculations lead to the classification of the one-dimensional ferrimagnetic behavior according to the constituent spins: the ferromagnetic ( $S > 2s$ ), antiferromagnetic ( $S < 2s$ ), and balanced ( $S = 2s$ ) ferrimagnetism.

**PACS.** 75.10.Jm Quantized spin models – 65.50.+m Thermodynamic properties and entropy – 75.40.Mg Numerical simulation studies

## 1 Introduction

One-dimensional quantum ferrimagnets are one of the hot topics and recent progress [1–15] in the theoretical understanding of them deserves special mention. Such a vigorous argument a great deal originates in the pioneering efforts to synthesize binuclear magnetic materials including one-dimensional systems. The first ferrimagnetic chain compound [16],  $\text{MnCu}(\text{dto})_2(\text{H}_2\text{O})_3 \cdot 4.5\text{H}_2\text{O}$  ( $\text{dto} = \text{dithiooxalato} = \text{S}_2\text{C}_2\text{O}_2$ ), was synthesized by Gleizes and Verdagner and stimulated the public interest in this potential subject. The following example of an ordered bimetallic chain [17],  $\text{MnCu}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$  ( $\text{pba} = 1,3\text{-propylenebis(oxamato)} = \text{C}_7\text{H}_6\text{N}_2\text{O}_6$ ), exhibiting more pronounced one dimensionality, further activated the physical [18,19], as well as chemical [20], investigations. There also appeared an idea [21] that the alternating magnetic centers do not need to be metal ions but may be organic radicals.

A practical model of a ferrimagnetic chain is two kinds of spins  $S$  and  $s$  ( $S > s$ ) alternating on a ring with antiferromagnetic exchange coupling between nearest neighbors, as described by the Hamiltonian,

$$\mathcal{H} = J \sum_{j=1}^N (\mathbf{S}_j \cdot \mathbf{s}_j + \mathbf{s}_j \cdot \mathbf{S}_{j+1}). \quad (1)$$

Here  $N$  is the number of unit cells and we set the unit-cell length equal to  $2a$  in the following. The simplest

case,  $(S, s) = (1, \frac{1}{2})$ , has so far been discussed fairly well. There lie both ferromagnetic and antiferromagnetic long-range orders in the ground state [2–4]. The ground state, which is a multiplet of spin  $(S - s)N$ , shows elementary excitations of two distinct types [8]. The excitations of ferromagnetic aspect, reducing the ground-state magnetization, form a gapless dispersion relation, whereas those of antiferromagnetic aspect, enhancing the ground-state magnetization, are gapped from the ground state. As a result of the low-energy structure of dual aspect, the specific heat shows a Shottky-like peak in spite of the ferromagnetic low-temperature behavior and the magnetic susceptibility times temperature exhibits a round minimum [3,10,18]. When the exchange coupling turns anisotropic, the dispersion of the ferromagnetic excitations is no more quadratic [1] and the plateau in the ground-state magnetization curve [12] due to the gapped antiferromagnetic excitations vanishes *via* the Kosterlitz-Thouless transition [15].

The quantum behavior of the model with higher spins is not yet so clear as that in the  $(S, s) = (1, \frac{1}{2})$  case. Though Drillon *et al.* [18] made the first attempt to reveal the general behavior of the model, they fixed the smaller spin to  $\frac{1}{2}$  in their argument with particular emphasis on the problem of the crystal engineering of a molecule-based ferromagnet—the assembly of the highly magnetic molecular entities within the crystal lattice in a ferromagnetic fashion. There also exists an extensive numerical study [3], but the leading attention was not necessarily directed to the consequences of the variation of the constituent spins.

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So far the generic behavior, rather than individual features, of ferrimagnetic mixed-spin chains has been accentuated or predicted, but there are few attempts to characterize or classify the typical one-dimensional ferrimagnetic behavior as a function of  $(S, s)$ . In such circumstances, we aim in this article at elucidating which property of the model (1) is universal and which one, if any, is variable with  $(S, s)$ .

It is true that numerical tools are quite useful in this context, but they are not almighty. Although the low-temperature ferromagnetic behavior is quite interesting from the experimental point of view, it is hardly feasible to numerically take grand-canonical averages at low enough temperatures. It is also unfortunate that with the increase of  $(S, s)$ , the available information is more and more reduced in both quality and quantity. Then we have an idea of describing the model in terms of the spin-wave theory. The conventional spin-wave treatment of low-dimensional magnets may discourage us. The Haldane conjecture [22] revealed a qualitative breakdown of the spin-wave description of one-dimensional Heisenberg antiferromagnets. Neither quantum corrections [23] nor additional constraints [24] to spin fluctuations end up with an overall scenario for the low-energy physics applicable to general spins. However, Ivanov [7] has recently reported that the spin-wave description of one-dimensional Heisenberg ferrimagnets is quite successful. Though his calculations were restricted to the ground-state energy and magnetization, the highly accurate estimates obtained there are surprising enough, considering the diverging ground-state magnetization in the one-dimensional antiferromagnetic spin-wave theory. For antiferromagnets, quantum fluctuations of domain-wall type, connecting the two degenerate Néel states, are important, whereas for ferrimagnets, domain-wall excitations lead to magnetization fluctuations and are thus of less significance. Therefore it is likely that the spin-wave approach is highly efficient for ferrimagnets. In an attempt to demonstrate such an idea, we try to describe not only the low-energy structure but also the thermal behavior of the Heisenberg ferrimagnetic spin chains (1) within the framework of the spin-wave theory. Extensive numerical calculations, supplemented by the spin-wave analysis, fully reveal the one-dimensional ferrimagnetic behavior as a function of the constituent spins.

## 2 Elementary excitations

In order to investigate the low-energy structure, we employ a new quantum Monte Carlo technique [25] as well as the conventional Lanczos diagonalization algorithm. The idea is in a word expressed as extracting the low-lying excitations from imaginary-time quantum Monte Carlo data at a low enough temperature. The imaginary-time correlation function  $S(q, \tau)$  is generally defined as

$$S(q, \tau) = \langle e^{\mathcal{H}\tau} O_q e^{-\mathcal{H}\tau} O_{-q} \rangle, \quad (2)$$

where  $O_q = N^{-1} \sum_{j=1}^N O_j e^{2iaqj}$  is the Fourier transform of an arbitrary local operator  $O_j$ , which may be

an effective combination of the spins  $\mathbf{S}$  and  $\mathbf{s}$ , and the thermal average at a given temperature  $\beta^{-1} = k_B T$ ,  $\langle A \rangle \equiv \text{Tr}[e^{-\beta\mathcal{H}} A] / \text{Tr}[e^{-\beta\mathcal{H}}]$ , is taken in a certain subspace.  $S(q, \tau)$  can be represented in terms of the eigenvectors and eigenvalues of the Hamiltonian,  $|l; k\rangle$  ( $l = 1, 2, \dots$ ) and  $E_l(k)$  ( $E_1(k) \leq E_2(k) \leq \dots$ ), and behaves like

$$S(q, \tau) \simeq \sum_l |\langle 1; k_0 | S_q^z | l; k_0 + q \rangle|^2 e^{-\tau[E_l(k_0+q) - E_1(k_0)]}, \quad (3)$$

at a sufficiently low temperature, where  $k_0$  is the momentum at which the lowest-energy state in the subspace is located. Therefore we can reasonably approximate  $E_1(k_0 + q) - E_1(k_0)$  by the slope  $-\partial \ln[S(q, \tau)] / \partial \tau$  in the large- $\tau$  region. When we take interest in the lower edge of the excitation spectrum, such a treatment is rather straightforward. The elementary excitations of the Haldane antiferromagnets were indeed revealed thus [26]. Here, due to the two kinds of spins in a chain and the resultant dual aspect of the low-energy structure, the relevant subspace and operator  $O_j$  are not uniquely defined. Since the total magnetization,  $M = \sum_j (S_j^z + s_j^z)$ , is a conserved quantity in the present system, we consider calculating  $S(q, \tau)$  independently in each subspace with a given  $M$  [27]. The elementary excitation energies for the ferromagnetic branch are obtained from a single calculation,  $S(q, \tau)$  in the subspace of  $M = 0$ , while those for the antiferromagnetic branch from a couple of calculations,  $S(q, \tau)$  and the lowest energy in the subspace of  $M = (S - s)N + 1$ . We have taken  $S_j^z \pm s_j^z$  for  $O_j$  and found that  $O_j = S_j^z - s_j^z$  extracts the eigenvalues of the bonding (lower-energy) states in both subspaces. The choice of the scattering matrices is a profound problem in itself and is fully discussed elsewhere [8, 28].

Although the chain length we can reach with the exact-diagonalization method is strongly limited, the diagonalization results are still helpful in the present system whose correlation length is generally so small as to be comparable to the unit-cell length (see Fig. 5). Actually, the ground-state energies for  $N = 10$  coincide with their thermodynamic-limit values within the first several digits. The Lanczos algorithm gives the most precise estimate for the ground-state energy and the antiferromagnetic excitation gap, whereas the quantum Monte Carlo technique is necessary for the evaluation of the curvature of the small-momentum dispersion.

On the other hand, we consider a spin-wave description of the elementary excitations as well. We introduce the bosonic operators for the spin deviation in each sublattice *via*

$$\begin{aligned} S_j^+ &= \sqrt{2S - a_j^\dagger a_j} a_j, & S_j^z &= S - a_j^\dagger a_j, \\ s_j^+ &= b_j^\dagger \sqrt{2s - b_j^\dagger b_j}, & s_j^z &= -s + b_j^\dagger b_j, \end{aligned} \quad (4)$$

where we regard  $S$  and  $s$  as quantities of the same order. The Hamiltonian (1) is expressed in terms of the bosonic operators as

$$\mathcal{H} = E_{\text{class}} + \mathcal{H}_0 + \mathcal{H}_1 + O(S^{-1}), \quad (5)$$

where  $E_{\text{class}} = -2sSJN$  is the classical ground-state energy, and  $\mathcal{H}_0$  and  $\mathcal{H}_1$  are the one-body and two-body terms of the order  $O(S^1)$  and  $O(S^0)$ , respectively. We may consider the simultaneous diagonalization of  $\mathcal{H}_0$  and  $\mathcal{H}_1$  in the naivest attempt to go beyond the noninteracting spin-wave theory. Indeed, the higher-order terms we take into account, the better description of the ground-state properties we obtain [7]. However, such an idea, as a whole, ends in failure, bringing a gap to the lowest-lying ferromagnetic excitation branch and thus qualitatively misreading the low-energy physics. Therefore, we take an alternative approach at the idea of first diagonalizing  $\mathcal{H}_0$  and next extracting relevant corrections from  $\mathcal{H}_1$ .  $\mathcal{H}_0$  is diagonalized as [3, 4]

$$\mathcal{H}_0 = E_0 + J \sum_k \left( \omega_k^- \alpha_k^\dagger \alpha_k + \omega_k^+ \beta_k^\dagger \beta_k \right), \quad (6)$$

where

$$E_0 = J \sum_k [\omega_k - (S + s)], \quad (7)$$

is the  $O(S^1)$  quantum correction to the ground-state energy, and  $\alpha_k^\dagger$  and  $\beta_k^\dagger$  are the creation operators of the ferromagnetic and antiferromagnetic spin waves of momentum  $k$  whose dispersion relations are given by

$$\omega_k^\pm = \omega_k \pm (S - s), \quad (8)$$

with

$$\omega_k = \sqrt{(S - s)^2 + 4Ss \sin^2(ak)}. \quad (9)$$

Using the Wick theorem,  $\mathcal{H}_1$  is rewritten as

$$\begin{aligned} \mathcal{H}_1 = & E_1 - J \sum_k \left( \delta\omega_k^- \alpha_k^\dagger \alpha_k + \delta\omega_k^+ \beta_k^\dagger \beta_k \right) \\ & + \mathcal{H}_{\text{irrel}} + \mathcal{H}_{\text{quart}}, \end{aligned} \quad (10)$$

where the  $O(S^0)$  correction to the ground-state energy,  $E_1$ , and those to the dispersions,  $\delta\omega_k^\pm$ , are, respectively, given by

$$E_1 = -2JN \left[ \Gamma_1^2 + \Gamma_2^2 + \left( \sqrt{S/s} + \sqrt{s/S} \right) \Gamma_1 \Gamma_2 \right], \quad (11)$$

$$\delta\omega_k^\pm = 2(S + s) \Gamma_1 \frac{\sin^2(ak)}{\omega_k} + \frac{\Gamma_2}{\sqrt{Ss}} [\omega_k \pm (S - s)], \quad (12)$$

with

$$\begin{aligned} \Gamma_1 &= \frac{1}{2N} \sum_k \left( \frac{S + s}{\omega_k} - 1 \right), \\ \Gamma_2 &= -\frac{1}{N} \sum_k \frac{\sqrt{Ss} \cos^2(ak)}{\omega_k}, \end{aligned} \quad (13)$$

while the irrelevant one-body terms

$$\mathcal{H}_{\text{irrel}} = -J \frac{(S - s)^2}{\sqrt{Ss}} \Gamma_1 \sum_k \frac{\cos(ak)}{\omega_k} (\alpha_k \beta_k + \alpha_k^\dagger \beta_k^\dagger), \quad (14)$$

and the residual two-body interactions  $\mathcal{H}_{\text{quart}}$  are both neglected so as to keep the ferromagnetic branch gapless. The resultant Hamiltonian is compactly represented as

$$\mathcal{H} \simeq E_g + J \sum_k \left( \tilde{\omega}_k^- \alpha_k^\dagger \alpha_k + \tilde{\omega}_k^+ \beta_k^\dagger \beta_k \right), \quad (15)$$

with

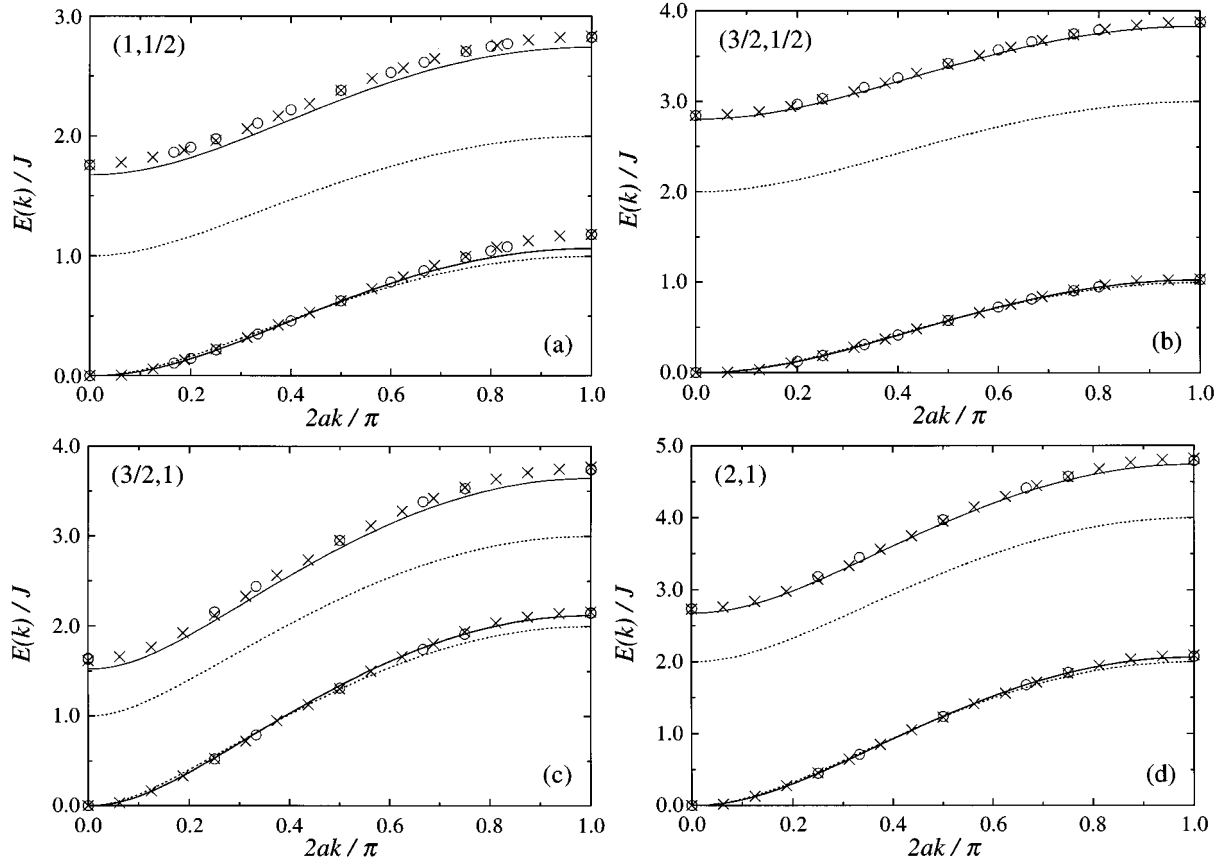
$$\tilde{\omega}_k^\pm = \omega_k^\pm - \delta\omega_k^\pm, \quad (16)$$

$$E_g = E_{\text{class}} + E_0 + E_1. \quad (17)$$

Now we compare all the calculations in Figure 1. The diagonalization results fully demonstrate the steady applicability and good precision of our Monte Carlo treatment. The spin-wave approach generally gives a good description of the low-energy structure. Even the free spin waves allow us to have a qualitative view of the elementary excitations. The relatively poor description of the antiferromagnetic branch by the free spin waves implies that the quantum effect is more relevant in the antiferromagnetic branch. Here we may be reminded of the spin-wave treatment of mono-spin Heisenberg magnets. For the ferromagnetic chains, the spin-wave dispersions are nothing but the exact picture of the elementary excitations, while for the antiferromagnetic chains, those are generally no more than a qualitative view. The point is that in the present system the spin-wave picture is efficient for both elementary excitation branches and the spin-wave series potentially lead to an accurate description. More specifically, the divergence of the boson numbers, which plagues the antiferromagnetic spin-wave treatment in one dimension, does not occur in the present system. This viewpoint is further discussed in the final section. We conclude this section by listing in Table 1 the spin-wave estimates of a few interesting quantities in comparison with the numerical solutions, where we define the curvature  $v$  as  $\tilde{\omega}_{k \rightarrow 0}^- = v(2ak)^2$ .

### 3 Thermodynamic properties

The dual structure of the excitations leads to unique thermal behavior. In order to complement quantum Monte Carlo thermal calculations, especially at low temperatures, we consider describing the thermodynamics in terms of the spin-wave theory. Introducing the additional constraint of the total magnetization being zero into the conventional spin-wave theory, Takahashi [29] succeeded in obtaining an excellent description of the low-temperature thermal behavior of one-dimensional Heisenberg ferromagnets. The present authors have recently applied the idea to the spin- $(1, \frac{1}{2})$  ferrimagnetic Heisenberg chain [10]. Here we develop the method for general spin cases and make a detailed analysis of its validity as a function of  $(S, s)$ . The core idea of the so-called modified spin-wave theory [30, 31] can be summarized as controlling the boson numbers by imposing a certain constraint on the magnetization. From this point of view, the zero-magnetization constraint, which is quite reasonable for isotropic magnets, plays a relevant role in ferromagnets.



**Fig. 1.** Dispersion relations of the ferromagnetic and antiferromagnetic elementary excitations, namely, the lowest-energy states in the subspaces of  $M = N/2 \mp 1$ . The noninteracting- and interacting-spin-wave calculations are shown by dotted and solid lines, respectively, whereas  $\times$  and  $\circ$  represent the quantum Monte Carlo estimates ( $N = 32$ ) and the exact-diagonalization results (up to  $N = 12$  (a), up to  $N = 10$  (b), up to  $N = 8$  (c, d)), respectively. Here we plot the excitation energy  $E(k)$  taking the ground-state energy as zero.

**Table 1.** Comparison between the linear-spin-wave (LSW), interacting-spin-wave (ISW), and numerical estimates of the ground-state energy  $E_g$ , the antiferromagnetic excitation gap  $\Delta$ , and the curvature of the ferromagnetic dispersion,  $v$ . The most accurate numerical estimates of  $E_g$  and  $\Delta$  are obtained by the exact diagonalization (Exact), whereas those of  $v$  by the quantum Monte Carlo (QMC).

$(S, s)$	$E_g/NJ$			$\Delta/J$			$v$		
	LSW	ISW	Exact	LSW	ISW	Exact	LSW	ISW	QMC
$(1, \frac{1}{2})$	-1.4365	-1.4608	-1.4541(1)	1	1.6756	1.759(1)	$\frac{1}{2}$	0.3804	0.37(1)
$(\frac{3}{2}, \frac{1}{2})$	-1.9580	-1.9698	-1.9672(1)	2	2.8025	2.842(1)	$\frac{3}{8}$	0.3390	0.31(1)
$(\frac{3}{2}, 1)$	-3.8281	-3.8676	-3.861(1)	1	1.5214	1.615(5)	$\frac{3}{2}$	1.1319	0.90(3)
$(2, 1)$	-4.8729	-4.8973	-4.893(1)	2	2.6756	2.730(5)	1	0.8804	0.76(2)

The resultant low-temperature expansions [29] of the specific heat and susceptibility of the spin- $s$  Heisenberg ferromagnetic chain,

$$\frac{C}{Nk_B} = \frac{3}{8s^{\frac{1}{2}}} \frac{\zeta(\frac{3}{2})}{\sqrt{\pi}} t^{\frac{1}{2}} - \frac{1}{2s^2} t + O(t^{\frac{3}{2}}), \quad (18)$$

$$\frac{\chi J}{N(g\mu_B)^2} = \frac{2s^4}{3} t^{-2} - s^{\frac{5}{2}} \frac{\zeta(\frac{1}{2})}{\sqrt{\pi}} t^{-\frac{3}{2}} + \frac{s}{2} \left[ \frac{\zeta(\frac{1}{2})}{\sqrt{\pi}} \right]^2 t^{-1} + O(t^{-\frac{1}{2}}), \quad (19)$$

with  $t = k_B T/J$  and Riemann's zeta function  $\zeta(z)$ , indeed coincide with the thermodynamic Bethe-ansatz calculations [32] for  $s = \frac{1}{2}$  within the leading few terms.

In the present system, the zero-magnetization constraint is explicitly represented as

$$\sum_j \langle S_j^z + s_j^z \rangle = (S - s)N - \sum_k \sum_{\sigma=\pm} \sigma \tilde{n}_k^{-\sigma} = 0, \quad (20)$$

where  $n_k^\pm = \sum_{n^-, n^+} n^\pm P_k(n^-, n^+)$  with  $P_k(n^-, n^+)$  being the probability of  $n^-$  ferromagnetic and  $n^+$  anti-ferromagnetic spin waves appearing in the  $k$ -momentum

state. Equation (20) straightforwardly proposes that the thermal spin deviation should cancel the Néel-state magnetization. By minimizing the free energy

$$F = E_g + \sum_k (\tilde{n}_k^- \tilde{\omega}_k^- + \tilde{n}_k^+ \tilde{\omega}_k^+) + k_B T \sum_k \sum_{n^-, n^+} P_k(n^-, n^+) \ln P_k(n^-, n^+), \quad (21)$$

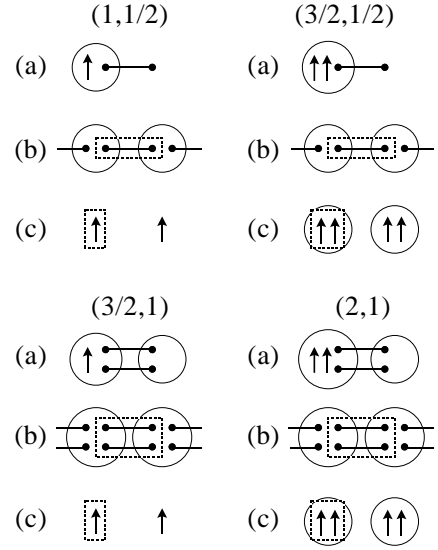
with respect to  $P_k(n^-, n^+)$  at each  $k$  under the condition (20) as well as the trivial constraints  $\sum_{n^-, n^+} P_k(n^-, n^+) = 1$ , we obtain

$$\frac{C}{Nk_B} = \frac{3}{4} \left( \frac{S-s}{Ss} \right)^{\frac{1}{2}} \frac{\zeta(\frac{3}{2}) \tilde{t}^{\frac{1}{2}}}{\sqrt{2\pi}} - \frac{1}{Ss} \tilde{t} + O(\tilde{t}^{\frac{3}{2}}), \quad (22)$$

$$\frac{\chi J}{N(g\mu_B)^2} = \frac{Ss(S-s)^2 \tilde{t}^{-2}}{3} - (Ss)^{\frac{1}{2}} (S-s)^{\frac{3}{2}} \frac{\zeta(\frac{1}{2}) \tilde{t}^{-\frac{3}{2}}}{\sqrt{2\pi}} + (S-s) \left[ \frac{\zeta(\frac{1}{2})}{\sqrt{2\pi}} \right]^2 \tilde{t}^{-1} + O(\tilde{t}^{-\frac{1}{2}}), \quad (23)$$

where  $\tilde{t} = k_B T / J\gamma$  with  $\gamma = 1 - \Gamma_1(S+s)/Ss - \Gamma_2/\sqrt{Ss}$ . The specific heat  $C$  has been obtained by differentiating the free energy  $F$ , whereas the susceptibility  $\chi$  by calculating  $(\langle M^2 \rangle - \langle M \rangle^2) / 3T$ , where we have set the  $g$  factors of the spins  $\mathbf{S}$  and  $\mathbf{s}$  both equal to  $g$ , because the difference between them amounts to at most several percent of themselves in practice [33].

The analytic expressions (22) and (23) give us a bird's-eye view of the one-dimensional ferrimagnetic behavior. The spin- $(S, s)$  ferrimagnet turns into the spin- $s$  antiferromagnet in the limit of  $S \rightarrow s$ , whereas it looks like the spin- $S$  ferromagnet in the limit of  $S/s \rightarrow \infty$ . In this sense, the subtraction  $S-s$  may be regarded as the ferromagnetic contribution, while the residual spin amplitude  $2s$  as the antiferromagnetic one. No ferromagnetic aspect at  $S/s = 1$ , while a hundred percent ferromagnetic aspect for  $S/s \rightarrow \infty$ . Another consideration also leads us to such a picture. Since the perturbation from the decoupled dimers [8] qualitatively well describes the low-lying excitations of the system, we propose in Figure 2 an idea of decomposing ferrimagnets into ferromagnets and antiferromagnets, where we let the decoupled dimers and the Affleck-Kennedy-Lieb-Tasaki valence-bond-solid states [34] symbolize ferrimagnets and integer-spin gapped antiferromagnets, respectively. Now we expect spin- $(S, s)$  ferrimagnets to behave like combinations of spin- $(2s)$  antiferromagnets and spin- $(S-s)$  ferromagnets. Since the antiferromagnetic excitations of the ferrimagnetic ground state are gapped, the low-temperature behavior of ferrimagnets should be only of ferromagnetic aspect. At low temperatures there is indeed no effective contribution from the spin- $(2s)$  antiferromagnetic chain with an excitation gap [22] immediately above the ground state. In this context, we are surprised but pleased to find that provided  $S = 2s$ , the expressions (22, 23) coincide with those for ferromagnets, (18) and (19), except for the quantum renormalizing factor  $\gamma$ . The low-temperature thermodynamics should be dominated by the small-momentum ferromagnetic



**Fig. 2.** Schematic representations of the  $M = (S - s)N$  ground states of spin- $(S, s)$  ferrimagnetic chains of  $N$  elementary cells in the decoupled-dimer limit (a), the AKLT ground states of spin- $(2s)$  antiferromagnetic chains of  $2N$  spins (b), the  $M = 2N(S - s)$  ground states of spin- $(S - s)$  ferromagnetic chains of  $2N$  spins (c). The arrow (the bullet symbol) denotes a spin  $1/2$  with its fixed (unfixed) projection value. The solid segment is a singlet pair. The circle represents an operation of constructing spins  $S$  and  $s$  by symmetrizing the spin  $1/2$ 's inside. The relation (a)  $\approx [(b) + (c)]/2$  may be expected.

excitations. Within the linearized spin-wave theory, the small-momentum dispersions of Heisenberg ferrimagnets and ferromagnets are characterized by the curvatures

$$v^{(S,s)\text{-ferri}} = \frac{Ss}{2(S-s)} J, \quad (24)$$

$$v^{(S-s)\text{-ferro}} = (S-s)J, \quad (25)$$

respectively, where we find that they coincide with each other only when  $S = 2s$ . The criterion,  $S = 2s$ , is further convincing when we consider the high-temperature behavior. The paramagnetic behavior of the spin- $(S, s)$  ferrimagnet is given as

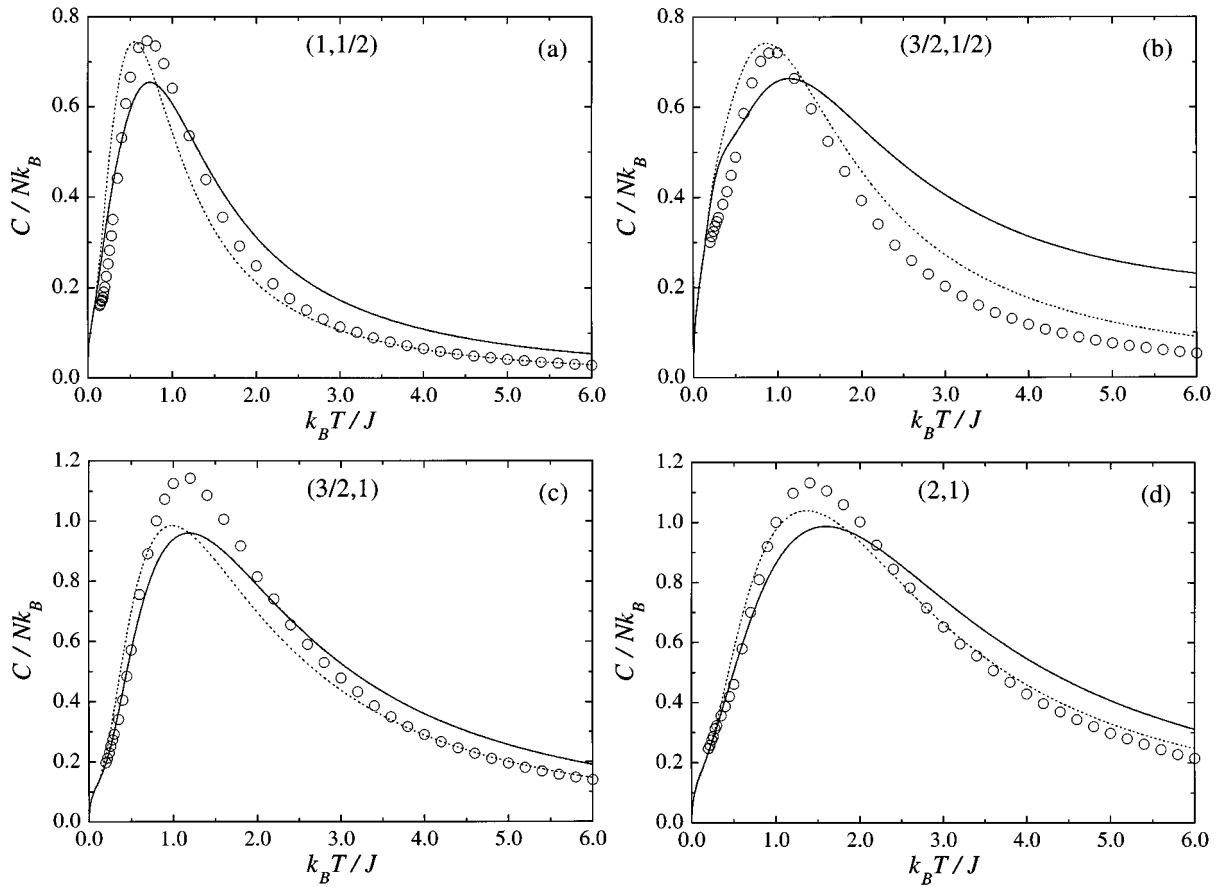
$$\frac{F^{(S,s)\text{-ferri}}}{Nk_B T} = -\ln[(2S+1)(2s+1)], \quad (26)$$

$$\frac{k_B T \chi^{(S,s)\text{-ferri}}}{Ng^2 \mu_B^2} = \frac{1}{3} [S(S+1) + s(s+1)], \quad (27)$$

whereas those of the spin- $(S-s)$  ferromagnet and the spin- $(2s)$  antiferromagnet are as follows:

$$\frac{F^{(S-s)\text{-ferro}} + F^{(2s)\text{-antiferro}}}{Nk_B T} = -\ln[(2S-2s+1)(4s+1)], \quad (28)$$

$$\frac{k_B T (\chi^{(S-s)\text{-ferro}} + \chi^{(2s)\text{-antiferro}})}{Ng^2 \mu_B^2} = \frac{1}{3} [(S-s)(S-s+1) + 2s(2s+1)]. \quad (29)$$



**Fig. 3.** Temperature dependences of the specific heat.  $\circ$  represents the quantum Monte Carlo estimates, whereas the solid line shows the modified-spin-wave calculations starting from the interacting-spin-wave dispersion relations.

These asymptotic values agree with each other only when  $S = 2s$ . This is simply the consequence of the degrees of freedom. In ferrimagnets of  $S > 2s$ , the ferromagnetic spin degrees of freedom overbalance the antiferromagnetic ones, while in ferrimagnets of  $S < 2s$ , *vice versa*. Only the balanced ferrimagnet with  $S = 2s$  is well-approximated as the simple combination of the spin- $(S - s)$  ferromagnet and the spin- $(2s)$  antiferromagnet. However, we note that even in the case of  $S = 2s$ , the similarity between the ferrimagnetic behavior, (22) and (23), and the ferromagnetic one, (18) and (19), does not go beyond the leading few terms shown here. The ferromagnetic features of ferrimagnets are thermally smeared out. On the other hand, the ferrimagnetic behavior further deviates from the purely ferromagnetic one due to the quantum effect characterized by  $\gamma$ . The low-temperature expansions (22, 23) imply that as temperature goes to zero, the quantum effect is reduced for the specific heat  $C$ , whereas enhanced for the susceptibility  $\chi$ . In the limit of  $S/s \rightarrow \infty$ , the quantum corrections  $\Gamma_1$  and  $\Gamma_2$  both vanish.

Although the spin-wave theory combined with the additional constraint (20) is so useful, it should further be modified at higher temperatures so as to control the total number of the bosons  $\sum_{\sigma=\pm} \tilde{n}_k^\sigma$  rather than the subtraction  $\sum_{\sigma=\pm} \sigma \tilde{n}_k^{-\sigma}$ . In our naivest attempt to improve the

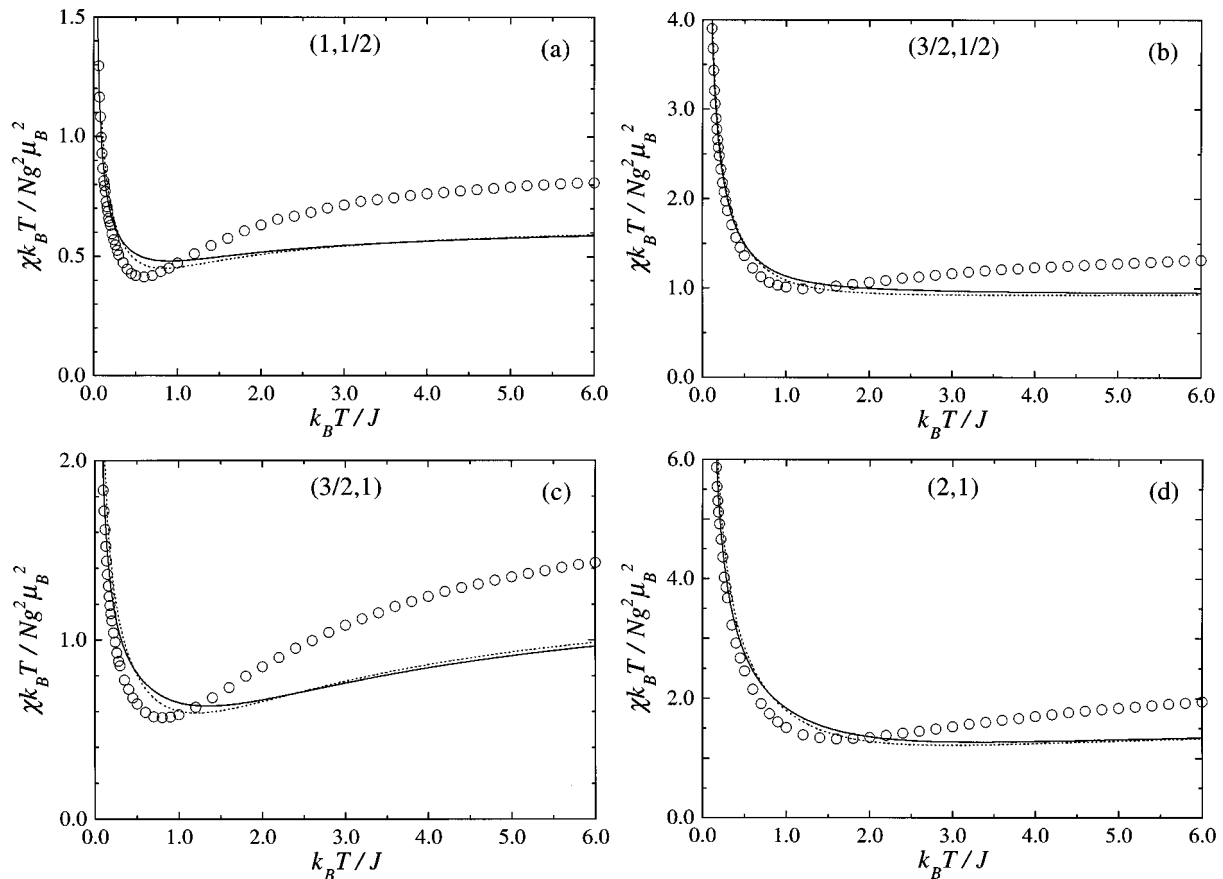
theory, we replace the constraint (20) by

$$\begin{aligned} \sum_j \langle S_j^z - s_j^z \rangle &= (S + s - 2\Gamma_1)N - (S + s) \sum_k \sum_{\sigma=\pm} \frac{\tilde{n}_k^\sigma}{\omega_k} \\ &= 0. \end{aligned} \quad (30)$$

However, the alternative condition (30) changes the low-temperature description, (22) and (23), which should be kept unchanged under any artificial constraint, as well as considerably underestimates the Schottky-like characteristic peak of the specific heat. In an attempt to remove  $\Gamma_1$  from equation (30), we reach a phenomenological modification

$$\begin{aligned} \sum_j \langle : S_j^z - s_j^z : \rangle &= (S + s)N - (S + s) \sum_k \sum_{\sigma=\pm} \frac{\tilde{n}_k^\sigma}{\omega_k} \\ &= 0, \end{aligned} \quad (31)$$

which proposes that the thermal fluctuation should cancel the Néel-state magnetization and results in the same low-temperature description as equations (22, 23), where the normal ordering is taken with respect to both operators  $\alpha$  and  $\beta$ . Now the overall description of the thermal quantities is numerically obtained and is shown, together with the precise quantum Monte Carlo calculations,



**Fig. 4.** Temperature dependences of the magnetic susceptibility times temperature.  $\circ$  represents the quantum Monte Carlo estimates, whereas the solid line shows the modified-spin-wave calculations starting from the interacting-spin-wave dispersion relations.

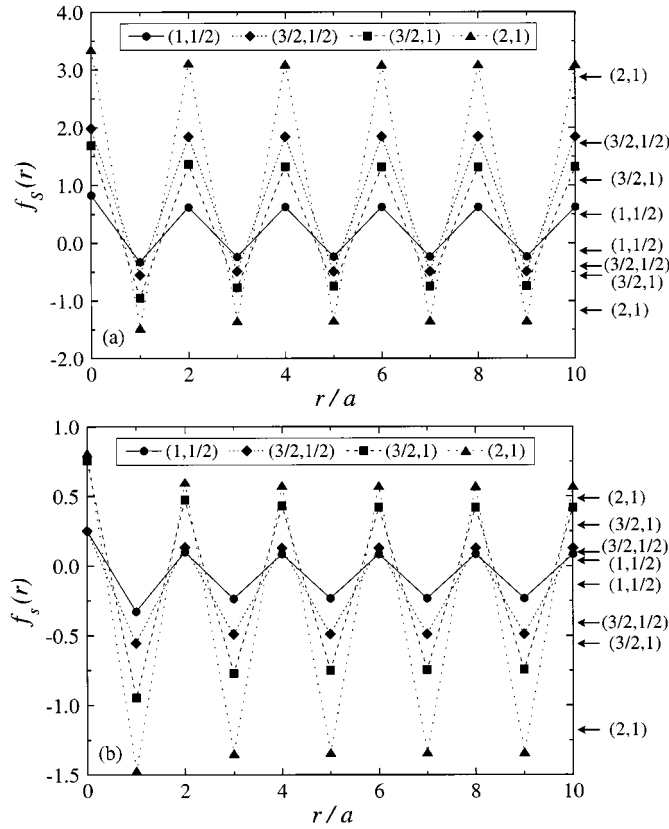
in Figures 3 and 4. We stress that these are the spin-wave description of one-dimensional magnets. We are allowed to recognize that the spin-wave picture is qualitatively valid even at high temperatures. The spin-wave theory, which is to overestimate the spin degrees of freedom, inevitably overestimates the energy-derivative quantities and under estimate the magnetization-derivative ones at high temperatures. However, the location of the Schottky-like peak of the specific heat is generally reproduced well, which should be attributed to the fine description of the antiferromagnetic excitation gap by the interacting spin waves. One might say that the spin-wave description is a overlikely portrait of the actual behavior. For the ferromagnetic ferrimagnet of  $(S, s) = (\frac{3}{2}, \frac{1}{2})$ , for instance, the low-temperature shoulder of  $C$  is too pronounced and the high-temperature antiferromagnetic increase of  $\chi T$  is too suppressed in the spin-wave theory. We note finally in this section that the double constraint does not improve the theory at all. At high temperatures, the constraint (31) dominates the thermal behavior but the constraint (20) works little. At low temperatures, where  $\tilde{n}_k^- \gg \tilde{n}_k^+$ , the two constraints (20) and (31) are almost degenerate and no numerical solution is found for the couple of Lagrange multipliers due to the double constraint. Further inclusion

of any tricky constraint is likely to make us lose sight of the physical basis.

## 4 Discussion

We have studied the low-energy structure and the thermal properties of Heisenberg ferrimagnetic spin chains featuring the spin-wave theory. Even with the modified spin-wave theory, it is still hard to describe the thermodynamics over the whole temperature range. However, considering the poor applicability of the spin-wave theory to one-dimensional antiferromagnets, the obtained description is quite successful. What is the difference between ferrimagnets and antiferromagnets, in spite of the antiferromagnetic coupling between nearest neighbors in common? The surprising efficiency of the present spin-wave treatment can be attributed to the ordered ground state [2] of ferrimagnets and thus to the nondiverging sublattice magnetization. The key constant  $\Gamma_1$  is nothing but the quantum spin reduction

$$\frac{1}{N} \sum_j \langle a_j^\dagger a_j \rangle_g = \frac{1}{N} \sum_j \langle b_j^\dagger b_j \rangle_g, \quad (32)$$



**Fig. 5.** Quantum Monte Carlo estimates of the longitudinal spin-correlation functions in the ground state with  $M = (S - s)N$ ; (a)  $f_S(r)$ : correlations between a larger spin and any other spin; (b)  $f_s(r)$ : correlations between a smaller spin and any other spin. The arrows indicate the  $r \rightarrow \infty$  asymptotic values obtained by the spin-wave theory.

where  $\langle A \rangle_g$  denotes the ground-state average of  $A$ .  $\Gamma_1$  monotonically decreases as  $S/s$  increases, diverging at  $S/s = 1$  and vanishing for  $S/s \rightarrow \infty$ . Since the spin reduction  $\Gamma_1$  can be a measure for the validity of the spin-wave description, the spin-wave theory in general works better as  $S/s$ , as well as  $Ss$ , increases.

In this context, it is interesting to observe the ground-state spin correlations,

$$f_S(r) = \begin{cases} S_j^z S_{j+l}^z & \text{for } r = 2la, \\ S_j^z s_{j+l}^z & \text{for } r = (2l+1)a, \end{cases} \quad (33)$$

$$f_s(r) = \begin{cases} s_j^z s_{j+l}^z & \text{for } r = 2la, \\ s_j^z S_{j+l+1}^z & \text{for } r = (2l+1)a. \end{cases} \quad (34)$$

Figure 5 shows the small- $r$  initial behavior of  $f_S(r)$  and  $f_s(r)$ , which demonstrates the considerably small correlation length and the existence of the long-range order in the present system. For the asymptotic correlation between the two larger spins far distant from each other, for example, the spin-wave estimate deviates from the actual value by 23%, 7%, 18%, and 7% for  $(S, s) = (1, \frac{1}{2})$ ,  $(\frac{3}{2}, \frac{1}{2})$ ,  $(\frac{3}{2}, 1)$ , and  $(2, 1)$ , respectively. We find that the above-defined

criterion in terms of  $S/s$  and  $Ss$  works fairly well. The theory is not so bad even in the extreme quantum case.

Quite recently, the nuclear spin relaxation time in a one-dimensional ferrimagnetic Heisenberg model compound,  $\text{NiCu}(\text{C}_7\text{H}_6\text{N}_2\text{O}_6)(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$ , has been measured [35] and its temperature and field dependences have successfully been interpreted within the framework of the spin-wave theory [36]. The theory must still be open to further applications to this fascinating system. We hope that the present study will motivate further explorations into low-dimensional ferrimagnets in both theoretical and experimental fields. The ferromagnetic and antiferromagnetic mixed nature may further be discussed from different points of view. For instance, the topological excitations such as instantons in ferromagnets and the topological terms in antiferromagnets might give further support to the present understanding of ferrimagnets.

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## References

1. F.C. Alcaraz, A.L. Malvezzi, J. Phys. Math. Gen. **30**, 767 (1997).
2. G.-S. Tian, Phys. Rev. B **56**, 5353 (1997).
3. S.K. Pati, S. Ramasesha, D. Sen, Phys. Rev. B **55**, 8894 (1997); J. Phys. Condens. Matter **9**, 8707 (1997).
4. S. Brehmer, H.-J. Mikeska, S. Yamamoto, J. Phys. Condens. Matter **9**, 3921 (1997).
5. T. Ono, T. Nishimura, M. Katsumura, T. Morita, M. Sugimoto, J. Phys. Soc. Jpn **66**, 2576 (1997).
6. H. Niggemann, G. Uimin, J. Zittartz, J. Phys. Condens. Matter **9**, 9031 (1997); **10**, 5217 (1998).
7. N.B. Ivanov, Phys. Rev. B **57**, 14024 (1998).
8. S. Yamamoto, S. Brehmer, H.-J. Mikeska, Phys. Rev. B **57**, 13610 (1998).
9. S. Yamamoto, T. Sakai, J. Phys. Soc. Jpn **67**, 3711 (1998).
10. S. Yamamoto, T. Fukui, Phys. Rev. B **57**, 14008 (1998); S. Yamamoto, T. Fukui, K. Maisinger, U. Schollwöck, J. Phys. Condens. Matter **10**, 11033 (1998).
11. K. Maisinger, U. Schollwöck, S. Brehmer, H.-J. Mikeska, S. Yamamoto, Phys. Rev. B **58**, 5908 (1998); A.K. Kolezhuk, H.-J. Mikeska, K. Maisinger, U. Schollwöck, Phys. Rev. B **59**, 13565 (1999).
12. T. Kuramoto, J. Phys. Soc. Jpn **67**, 1762 (1998); **68**, 1813 (1999).
13. S. Yamamoto, Phys. Rev. B **59**, 1024 (1999).
14. C. Wu, B. Chen, X. Dai, Y. Yu, Z.-B. Su, Phys. Rev. B **60**, 1057 (1999).
15. T. Sakai, S. Yamamoto, Phys. Rev. B **60**, 4053 (1999); S. Yamamoto, T. Sakai, J. Phys. Condens. Matter **11**, 5175 (1999).



16. A. Gleizes, M. Verdaguer, *J. Am. Chem. Soc.* **103**, 7373 (1981); **106**, 3727 (1984).
17. Y. Pei, M. Verdaguer, O. Kahn, J. Sletten, J.-P. Renard, *Inorg. Chem.* **26**, 138 (1987).
18. M. Drillon, J.C. Gianduzzo, R. Georges, *Phys. Lett. A* **96**, 413 (1983); M. Drillon, E. Coronado, R. Georges, J.C. Gianduzzo, J. Curely, *Phys. Rev. B* **40**, 10992 (1989).
19. M. Verdaguer, A. Gleizes, J.-P. Renard, J. Seiden, *Phys. Rev. B* **29**, 5144 (1984).
20. O. Kahn, Y. Pei, M. Verdaguer, J.-P. Renard, J. Sletten, *J. Am. Chem. Soc.* **110**, 782 (1988); P.J. van Koningsbruggen, O. Kahn, K. Nakatani, Y. Pei, J.-P. Renard, M. Drillon, P. Legoll, *Inorg. Chem.* **29**, 3325 (1990).
21. A. Caneschi, D. Gatteschi, P. Rey, R. Sessoli, *Inorg. Chem.* **27**, 1756 (1988); A. Caneschi, D. Gatteschi, J.-P. Renard, P. Rey, R. Sessoli, *ibid.* **28**, 1976 (1989); 2940 (1989).
22. F.D.M. Haldane, *Phys. Lett. A* **93**, 464 (1983); *Phys. Rev. Lett.* **50**, 1153 (1983).
23. T. Oguchi, *Phys. Rev.* **117**, 117 (1960).
24. S.M. Rezende, *Phys. Rev. B* **42**, 2589 (1990).
25. S. Yamamoto, *Int. J. Mod. Phys. C* **8**, 609 (1997).
26. S. Yamamoto, *Phys. Rev. Lett.* **75**, 3348 (1995).
27. S. Yamamoto, S. Miyashita, *Phys. Lett. A* **235**, 545 (1997).
28. S. Yamamoto, *Phys. Rev. B* **51**, 16128 (1995).
29. M. Takahashi, *Phys. Rev. Lett.* **58**, 168 (1987).
30. M. Takahashi, *Phys. Rev. B* **40**, 2494 (1989).
31. J.E. Hirsch, S. Tang, *Phys. Rev. B* **40**, 4769 (1989); S. Tang, M.E. Lazzouni, J.E. Hirsch, *Phys. Rev. B* **40**, 5000 (1989).
32. M. Takahashi, M. Yamada, *J. Phys. Soc. Jpn* **54**, 2808 (1985); M. Yamada, M. Takahashi, *ibid.* **55**, 2024 (1986).
33. M. Hagiwara, K. Minami, Y. Narumi, K. Tatani, K. Kindo, *J. Phys. Soc. Jpn* **67**, 2209 (1998).
34. I. Affleck, T. Kennedy, E.H. Lieb, H. Tasaki, *Phys. Rev. Lett.* **59**, 799 (1987); *Commun. Math. Phys.* **115**, 477 (1988).
35. N. Fujiwara, M. Hagiwara, to be published in *Solid State Commun.*
36. S. Yamamoto, *Phys. Rev. B* **61**, 842 (2000).